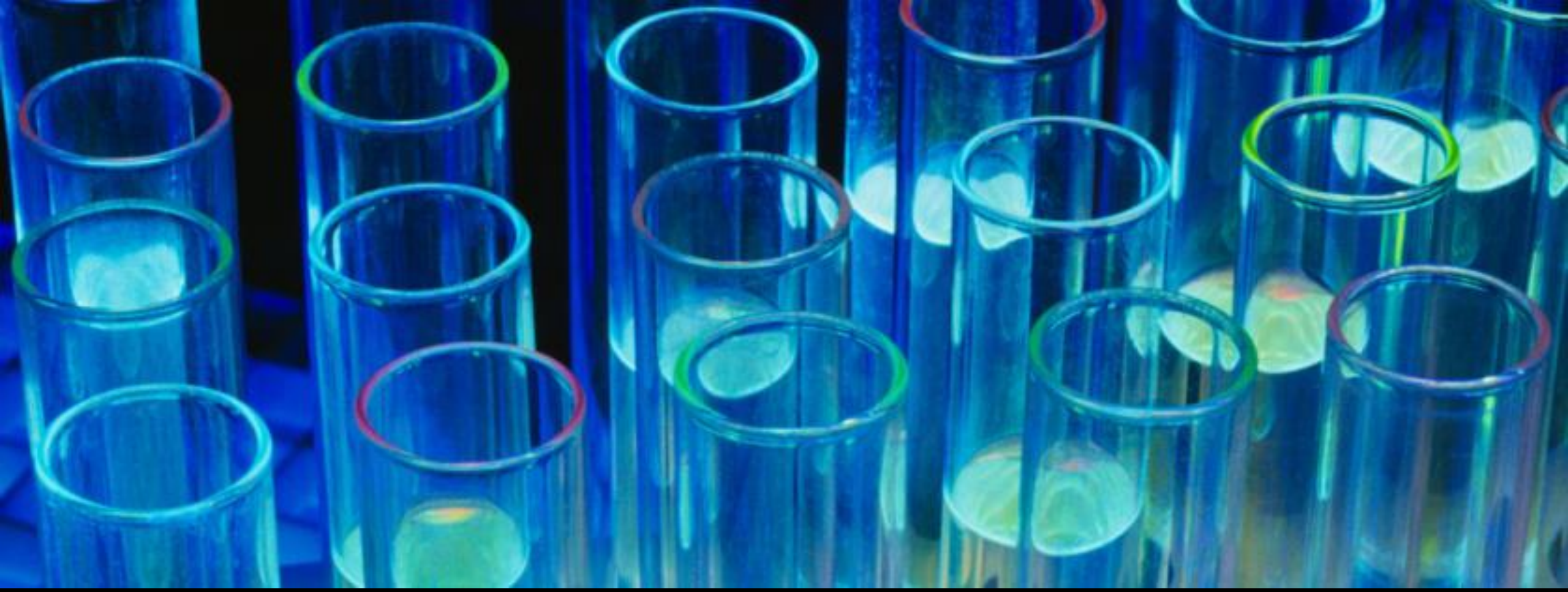


Modifications in the Extraction of Water Samples for Method 625

John Giles

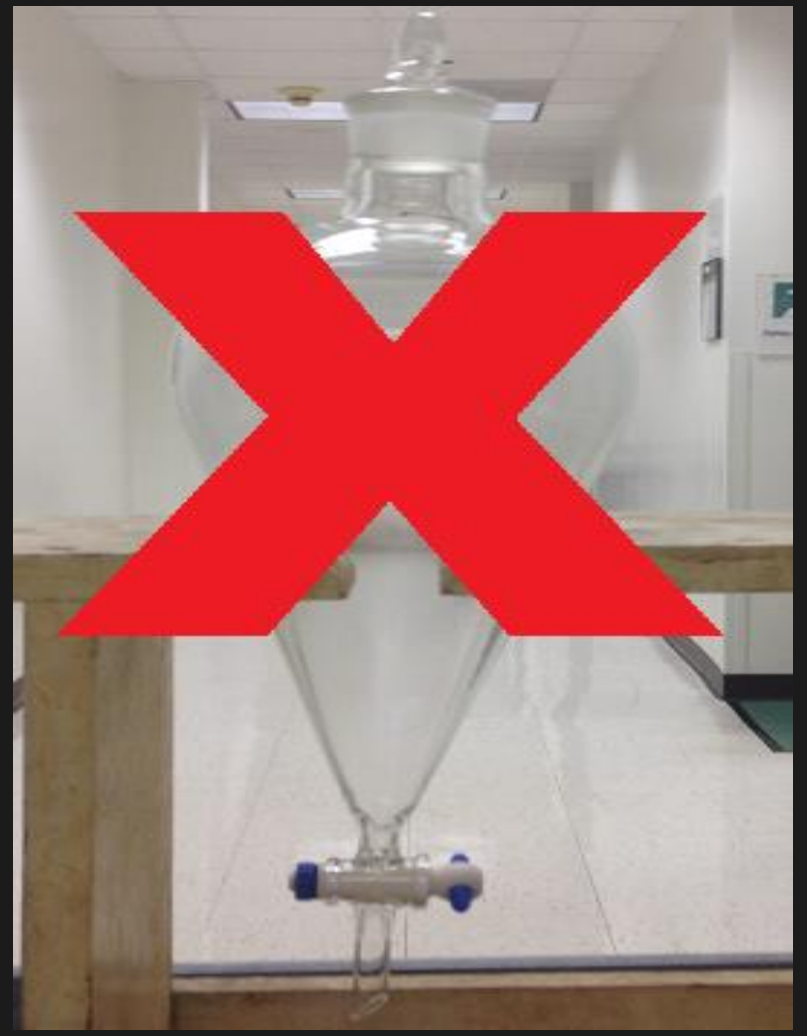
Method 625: The Extraction

- Currently, samples are extracted by either separatory funnel or CLLE.

- What's more achievable to a lab – "greenness" or time?
  - Sep funnel = time
  - CLLE = green

Why Not Separatory Funnel?

- Separatory funnel *much* faster, but…
  - Uses large volume of CH_2Cl_2: (3 x 60 mL acid extract + 3 x 60 mL base extract = **<u>360 mL</u>** solvent)
  - Could form emulsions difficult to separate
  - For our laboratory, 625 projects are infrequent.



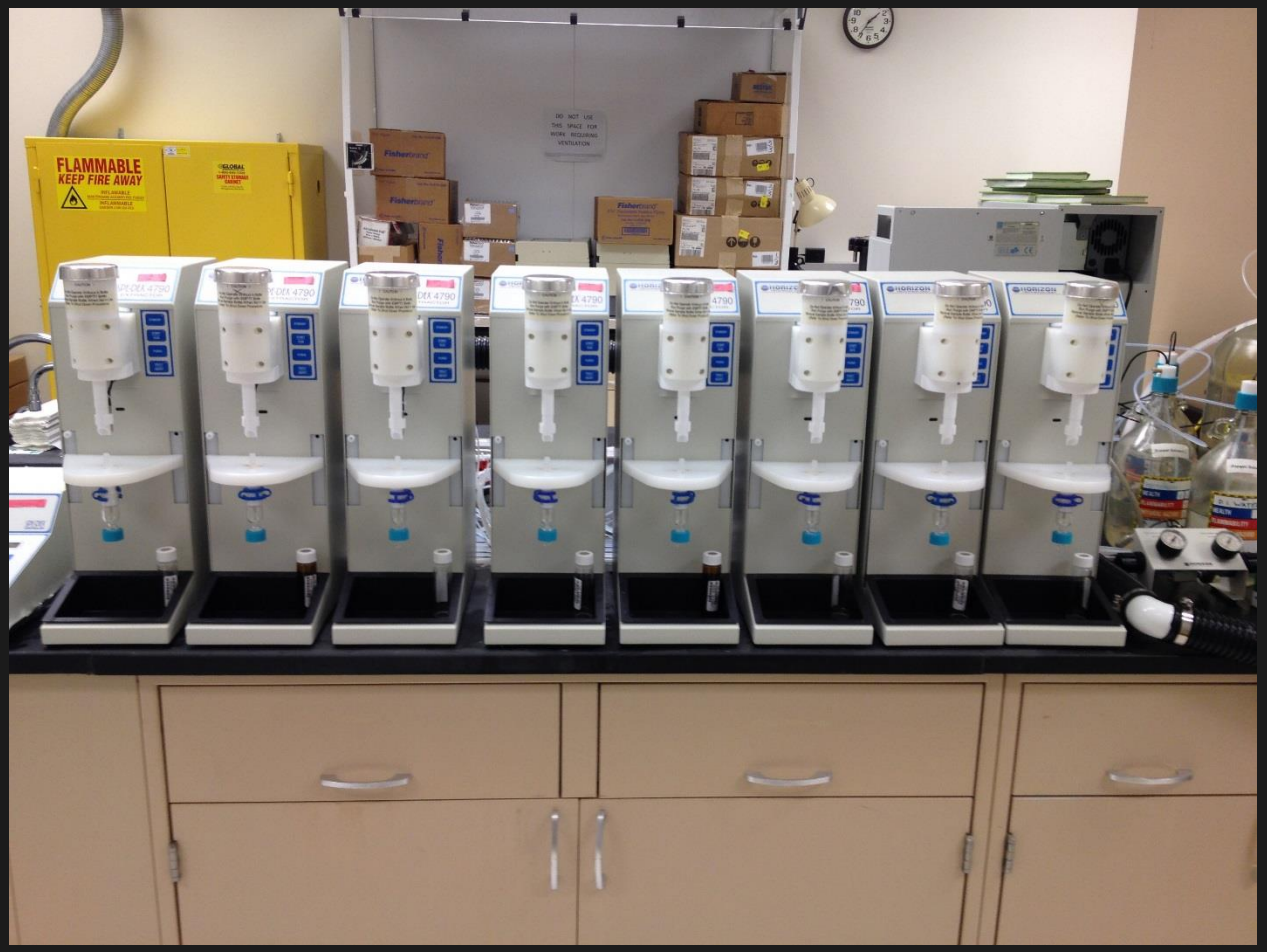
Pros/Cons of CLLE in Method 625

- CH_2Cl_2 volume reduced to slightly > 100 mL
- Design of apparatus means no emulsions or drying of extract
- But… total extraction process is over **48 hours** in length
  - Could factor in low recovery of some analytes
  - Experience with Method 3520 show that 24 hours is not necessary
- Method 625.1 to the rescue!

Updates in Method 625.1

- Should be promulgated later in 2015-16, includes SPE as alternate extraction technique
- From Sections 10.3.4 and 10.3.5 in 625.1: "*…extract for 18 – 24 hours. A longer or shorter extraction time may be used if all QC acceptance criteria are met.*"
- DOC: 6 hours @ pH 2, 6+ hours @ pH 11, completed Feb. 2015
- MDL study: Same conditions as DOC, completed April 2015

Method 625.1 – SPE Capable



- Our lab has SPE modules capable for Method 625.1
- However, they are exclusively used for Method 525.2 (drinking water) at the moment.

Initial Demonstration of Capability
Method 625, Precision and Accuracy Study
John Giles, February 12, 2015

Compound	Spike µg/L	BS1 µg/L	BS2 µg/L	BS3 µg/L	BS4 µg/L	BS5 µg/L	Std. Dev. µg/L	Avg. µg/L	%RSD	Avg. % Rec	Acceptance Criteria
N-Nitrosodimethylamine	100.00	56.61	72.42	81.79	60.62	82.98	12.01	70.88	16.94%	70.9%	49-93
bis(2-Chloroethyl)ether	100.00	53.54	66.24	76.99	56.64	78.13	11.30	66.31	17.04%	66.3%	12-158
Phenol	100.00	51.75	62.05	68.53	52.36	70.80	8.86	61.10	14.50%	61.1%	10-112
2-Chlorophenol	100.00	53.07	66.06	75.09	55.32	78.55	10.86	65.22	16.66%	65.2%	23-134
bis(2-chloroisopropyl)ether	100.00	51.55	61.62	69.77	52.51	69.94	8.85	61.14	14.48%	61.1%	36-166
Hexachloroethane	100.00	36.67	56.27	64.47	46.38	65.54	12.31	53.87	22.85%	53.9%	40-113
N-Nitroso-di-n-propylamine	100.00	52.73	63.07	69.96	55.75	71.90	8.44	62.68	13.47%	62.7%	10-230
Nitrobenzene	100.00	49.90	59.82	66.72	52.64	69.81	9.06	60.18	15.06%	60.2%	35-180
Isophorone	100.00	51.00	59.32	66.39	54.01	68.15	7.49	59.77	12.53%	59.8%	21-196
2-Nitrophenol	100.00	54.37	66.65	75.87	57.49	77.74	10.52	66.22	15.89%	66.2%	29-182
2,4-Dimethylphenol	100.00	49.75	59.33	67.51	52.51	68.96	8.62	59.61	14.47%	59.6%	32-119
bis(2-Chloroethoxy)methane	100.00	51.82	61.63	70.24	55.10	71.47	8.79	62.05	14.16%	62.1%	33-184
2,4-Dichlorophenol	100.00	54.87	65.41	73.96	57.97	76.68	9.56	65.78	14.54%	65.8%	39-135
Naphthalene	100.00	46.90	56.38	63.69	50.49	63.54	7.54	56.18	13.43%	56.2%	21-133
Hexachlorobutadiene	100.00	38.90	54.73	64.16	46.97	65.25	11.27	54.00	20.86%	54.0%	24-116
4-Chloro-3-methylphenol	100.00	64.39	70.65	79.00	66.42	79.77	7.08	72.05	9.82%	72.0%	22-147
Hexachlorocyclopentadiene	100.00	37.65	52.97	58.37	44.96	63.87	10.45	51.56	20.27%	51.6%	10-133
2,4,6-Trichlorophenol	100.00	63.63	73.01	80.78	66.95	82.19	8.20	73.31	11.18%	73.3%	37-144
2-Chloronaphthalene	100.00	52.02	61.92	68.19	56.78	69.16	7.34	61.61	11.92%	61.6%	60 118
Acenaphthylene	100.00	55.06	61.71	67.53	56.04	66.87	5.43	61.84	8.79%	61.8%	33-145
Dimethylphthalate	100.00	67.81	70.10	76.06	68.15	74.60	3.78	71.34	5.29%	71.3%	10-112
2,6-Dinitrotoluene	100.00	75.94	78.87	86.97	78.96	84.53	4.54	81.05	5.60%	81.1%	50-158
Acenaphthene	100.00	58.23	65.79	72.43	61.80	72.29	6.30	66.11	9.53%	66.1%	47 145
2,4-Dinitrophenol	200.00	197.87	202.05	221.47	213.14	223.74	11.54	211.61	5.45%	105.8%	10-191
2,4-Dinitrotoluene	100.00	84.94	84.23	91.34	86.79	89.07	2.95	87.27	3.38%	87.3%	39-139
4-Nitrophenol	100.00	89.08	88.84	94.26	87.03	91.73	2.77	90.37	3.06%	90.4%	10-132
Fluorene	100.00	62.97	68.16	74.63	65.90	73.21	4.90	68.97	7.11%	69.0%	59-121
4-Chlorophenyl-phenylether	100.00	67.95	74.73	81.42	71.94	80.09	5.61	75.23	7.46%	75.2%	25-158
Diethylphthalate	100.00	72.17	71.71	78.31	72.56	75.69	2.83	74.09	3.82%	74.1%	10-114
4,6-Dinitro-2-methylphenol	100.00	107.09	108.94	116.03	111.66	115.26	4.33	111.39	3.89%	111.4%	10-181
n-Nitrosodiphenylamine	100.00	70.68	72.90	76.10	71.90	75.51	2.33	73.42	3.17%	73.4%	62-89
1,2-Diphenylhydrazine	100.00	59.68	63.87	66.71	61.23	66.51	3.13	63.60	4.92%	63.6%	61-117
4-Bromophenyl-phenylether	100.00	75.16	79.73	85.74	78.98	85.02	4.43	80.93	5.47%	80.9%	53-127
Hexachlorobenzene	100.00	77.12	79.63	83.14	80.54	83.43	2.62	80.77	3.24%	80.8%	10 152
Pentachlorophenol	100.00	98.30	99.80	106.53	102.09	103.43	3.21	102.03	3.14%	102.0%	14-176
Phenanthrene	100.00	67.85	69.28	72.02	69.16	70.48	1.57	69.76	2.25%	69.8%	54-120
Anthracene	100.00	66.72	69.13	71.55	68.68	69.59	1.74	69.13	2.51%	69.1%	27-133
Di-n-butylphthalate	100.00	67.67	67.62	71.19	67.45	68.79	1.57	68.54	2.29%	68.5%	10 118
Fluoranthene	100.00	73.29	73.41	77.48	74.34	75.17	1.71	74.74	2.29%	74.7%	26-137
Benzidine	100.00	41.10	41.11	48.16	39.23	45.79	3.73	43.08	8.67%	43.1%	10-192
Pyrene	100.00	70.81	70.89	72.56	72.13	73.96	1.30	72.07	1.81%	72.1%	52-115
Butylbenzylphthalate	100.00	75.18	74.45	77.82	76.38	78.25	1.64	76.42	2.14%	76.4%	10-152
3,3'-Dichlorobenzidine	100.00	76.85	71.43	79.81	75.60	77.19	3.05	76.14	4.01%	76.1%	10 262
Benzo[a]anthracene	100.00	77.52	77.88	81.90	79.88	80.72	1.86	79.58	2.34%	79.6%	33 143
Chrysene	100.00	77.88	78.32	81.32	79.85	80.51	1.45	79.58	1.83%	79.6%	17-168
bis(2-Ethylhexyl)phthalate	100.00	73.05	72.80	76.04	73.77	76.66	1.77	74.46	2.38%	74.5%	10-158
Di-n-octylphthalate	100.00	70.95	70.80	73.18	71.36	73.38	1.25	71.93	1.73%	71.9%	10-146
Benzo[b]fluoranthene	100.00	92.32	93.06	92.80	91.26	93.93	0.98	92.67	1.06%	92.7%	24-159
Benzo[k]fluoranthene	100.00	70.68	78.87	77.27	77.86	74.82	3.28	75.90	4.32%	75.9%	11-162
Benzo[a]pyrene	100.00	80.04	82.36	85.54	83.73	83.30	2.02	82.99	2.43%	83.0%	17-163
Indeno[1,2,3-cd]pyrene	100.00	86.51	86.81	89.39	83.89	82.21	2.78	85.76	3.24%	85.8%	10-171
Dibenz[a,h]anthracene	100.00	84.53	85.29	87.40	82.18	79.99	2.86	83.88	3.42%	83.9%	10-227
Benzo[g,h,i]perylene	100.00	85.69	85.91	88.34	82.02	79.84	3.39	84.36	4.02%	84.4%	10 219

Data for DOC

- All analytes meet 625 acceptance criteria limits
- Standard deviation for all analytes no greater than 12.3 µg/L
  - For reference, the *lowest* standard deviation listed for any analyte is 13.0 µg/L
  - All RSD values 22.8% or less
- Analyte list based on TTO (Total Toxic Organics)

MDL Study for Method 625 – Part 1

- Originally performed along with DOC in February, spiked at 1.0 µg/L
- Most analytes passed the stringent MDL requirements
  - The few that failed had MDLs < 0.1 x MRL
  - 40 CFR Part 136, Appendix B stipulates 0.1X MRL ≤ MDL ≤ MRL

MDL Study for Method 625 – Part 2

- Most analytes on TTO list have MRL ≥ 10 µg/L
- Our MRLs set to either 5 or 10 µg/L, depending on MRLs listed for TTOs.
- Repeated study in April
  - Analytes spiked at 10 µg/L
  - This time, all passed MDL requirements

Conclusions

- Our extraction technique results in less solvent and time used
- DOC/MDL data show consistent recoveries

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